

10 Electrostatic and Electrokinetic Phenomena

Our discussion so far has avoided the cases involving electrolytic solutions. Non-electrolytes have no effect on sols and suspensions. In reality, however, many disperse systems which we encounter contain electrolytes and the stability of the dispersion is due to electrostatic effects. An important cause of dispersion instability is aggregation and flocculation. Clay particles (usually negatively charged) and silt carried in suspensions by rivers are electrically charged to repel each other, but coagulate upon encountering salt sea and form huge deltas. Electrostatic stabilization is also responsible for the long shelf-life of certain latex paints. Electrostatic forces governs the behavior of biological systems.

When charged particles are under an electric field, they move in a dispersion medium, which is usually an electrolyte. When there is a relative motion between the particles and the medium, the phenomena observed include electrophoresis, electroosmosis, streaming potential, sedimentation potential, etc. The technique of electrophoresis is widely used in measuring the charge on a particle. The electric conductivity of a suspension reflects electrokinetic processes.

10.1 The Electric Stress Tensor in a Compressible Fluid

In order to understand the interaction forces among particles in an electrolyte solution, we must discuss the electric stress tensor. Let us consider an electrostatic field, \mathbf{E} , arising from charges located on the surfaces of conductors embedded in an isotropic dielectric or an electrolyte solution. We assume that the dielectric is continuous outside the conductors and the dielectric constant, ϵ , depends on position. The total electrostatic energy of the system is then given by a well-known expression:

$$U = \frac{1}{2} \int \epsilon_0 \epsilon E^2 dV, \quad (\mathbf{E} = 0, \text{ inside conductors}) \quad (10.1)$$

Now suppose that the dielectric is, at every point, subject to an arbitrary, infinitesimal displacement \mathbf{s} , which gives rise to a volume change, from dV_1 to dV_2 , given by

$$dV_2 = (1 + \nabla \cdot \mathbf{s})dV_1 \quad (10.2)$$

Because of this volume change, the density changes from ρ_1 to ρ_2 . Since the mass should be conserved, $\rho_1 dV_1 = \rho_2 dV_2$. Therefore,

$$d\rho = \rho_2 - \rho_1 = -\rho \nabla \cdot \mathbf{s}, \quad (\rho_2 \equiv \rho) \quad (10.3)$$

Hence, the dielectric constant, ε , changes due to two reasons: one is because of $d\rho$ of Eq. 10.3 and another is due to the displacement \mathbf{s} of the dielectric, $\varepsilon(\mathbf{x}-\mathbf{s}) \rightarrow \varepsilon(\mathbf{x})$ at position \mathbf{x} . Thus,

$$\delta\varepsilon = -\mathbf{s} \cdot \nabla \varepsilon + \frac{\partial \varepsilon}{\partial \rho} d\rho = -\mathbf{s} \cdot \nabla \varepsilon - \rho \frac{\partial \varepsilon}{\partial \rho} \nabla \cdot \mathbf{s} \quad (10.4)$$

This change of ε results in the change in the electrostatic energy:

$$dU = -\frac{1}{2}\varepsilon_0 \int \delta\varepsilon E^2 dV = \frac{1}{2}\varepsilon_0 \int E^2 (\nabla \varepsilon \cdot \mathbf{s} + \rho \frac{\partial \varepsilon}{\partial \rho} \nabla \cdot \mathbf{s}) dV \quad (10.5)$$

Or,

$$dU = \int \frac{1}{2}\varepsilon_0 \left[E^2 \nabla \varepsilon - \nabla \left(E^2 \rho \frac{\partial \varepsilon}{\partial \rho} \right) \right] \cdot \mathbf{s} dV + \int \frac{1}{2}\varepsilon_0 \nabla \cdot \left(E^2 \rho \frac{\partial \varepsilon}{\partial \rho} \mathbf{s} \right) dV \quad (10.5b)$$

The last integral can be changed, by the divergence theorem, to a surface integral over the interfaces of the conductors. This integral, therefore, must vanish because there are no displacements in the conductors and $\mathbf{s}=0$ at the surfaces by assumption.

When the displacement \mathbf{s} occurs due to an electric force, \mathbf{F} , per unit volume in the solution, there is a work done by this force and from the law of conservation of energy the energy of the field must decrease. If we neglect the gravitational and other mechanical forces, the work done by \mathbf{F} is given by

$$\int \mathbf{F} \cdot \mathbf{s} dV = - \int \frac{1}{2}\varepsilon_0 \left[E^2 \nabla \varepsilon - \nabla \left(E^2 \rho \frac{\partial \varepsilon}{\partial \rho} \right) \right] \cdot \mathbf{s} dV \quad (10.6)$$

Since this must hold for any arbitrary \mathbf{s} , the force per unit volume can be given by

$$\mathbf{F} = -\frac{1}{2}\varepsilon_0 E^2 \nabla \varepsilon + \frac{1}{2}\varepsilon_0 \nabla \left(E^2 \rho \frac{\partial \varepsilon}{\partial \rho} \right) \quad (10.7)$$

This is called a body force and behaves like a vector under a coordinate transformation.

If the dielectric constant is uniform and does not deform under \mathbf{E} , there is no electric body force, \mathbf{F} , unless free charges (ions) are distributed in the solution. If the net free charge density is denoted by ρ_f , then since $\rho_f = \epsilon_0 \nabla \cdot \epsilon \mathbf{E}$ and $(\nabla \cdot \epsilon \mathbf{E}) \mathbf{E} = \nabla \cdot (\epsilon \mathbf{E} \mathbf{E}) - (1/2) \epsilon \nabla E^2$ for an electrostatic field, the body force is given by

$$\mathbf{F} = \epsilon_0 \nabla \cdot (\epsilon \mathbf{E} \mathbf{E}) - \frac{1}{2} \epsilon_0 \nabla (\epsilon E^2) + \frac{1}{2} \epsilon_0 \nabla \left(E^2 \rho \frac{\partial \epsilon}{\partial \rho} \right) \quad (10.8)$$

To a good approximation, the Clausius-Mossotti law holds here. Then, from Eq. 4.90, we find that

$$\frac{\epsilon - 1}{\epsilon + 2} = C\rho \quad (10.9)$$

where C is a constant depending on the other properties, such as the molecular weight, of the dielectric. Using Eq. 10.9, we have

$$\mathbf{F} = \epsilon_0 \nabla \cdot (\epsilon \mathbf{E} \mathbf{E}) - \epsilon_0 \nabla \left[\frac{1}{2} \epsilon E^2 - \frac{1}{6} (\epsilon - 1)(\epsilon + 2) E^2 \right] \quad (10.10)$$

Now, in order to understand how the body force can exert a stress on a surface in the dielectric, consider that the dielectric is an elastic body, in which a stress is distributed. Let us apply the divergence theorem to the stress, denoted by $\overleftrightarrow{\tau}$. If a volume V is enclosed by a closed surface S with outward unit vector \mathbf{n} , we have

$$\oint_S \overleftrightarrow{\tau} \cdot \mathbf{n} dS = \int_V \nabla \cdot \overleftrightarrow{\tau} dV \quad (10.11)$$

If $\overleftrightarrow{\tau}$ is a stress tensor, $\overleftrightarrow{\tau} \cdot \mathbf{n} dS$ is the normal force acting on dS . Since this normal force is integrated over S , the left-hand side corresponds to the total force acting on the volume V . Therefore, from the right-hand side $\nabla \cdot \overleftrightarrow{\tau}$ must be a body force per unit volume. We can identify this body force by \mathbf{F} of Eq. 10.8, i.e., $\mathbf{F} = \nabla \cdot \overleftrightarrow{\tau}$. Therefore, we can write

$$\overleftrightarrow{\tau} = \epsilon_0 \epsilon \left[\mathbf{E} \mathbf{E} - \frac{1}{2} \left(1 - \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho} \right) E^2 \overleftrightarrow{\mathbf{I}} \right], \quad (10.12)$$

where $\overleftrightarrow{\mathbf{I}}$ is the unit dyadic ($\mathbf{i}\mathbf{i} + \mathbf{j}\mathbf{j} + \mathbf{k}\mathbf{k}$). Therefore, we find that the α component of the electric force acting on a surface with a normal unit vector, $\mathbf{n} = (n_x, n_y, n_z)$, is given by

$$\sum_{\beta} \tau_{\alpha\beta} n_{\beta} = \epsilon_0 \epsilon \left[\sum_{\beta} E_{\alpha} E_{\beta} n_{\beta} - \frac{1}{2} \left(1 - \frac{\rho}{\epsilon} \frac{\partial \epsilon}{\partial \rho} \right) E^2 n_{\alpha} \right] \quad (10.13)$$

where $\alpha, \beta = x, y, z$. Using Eq. 10.13 we can find a force acting on a conductor which is immersed in the dielectric.

In equilibrium, the electric body force must be balanced by a mechanical body force, like an osmotic body force, ∇p , due to an osmotic pressure p originating in the distribution of ions (see Sec. 10.3).

10.2 Ions in Liquid Dielectric and Electric Double Layer

In an electrolyte solution, ions may be produced by dissociations:



The relative concentrations of ions, $[\text{A}^-]$ and $[\text{H}^+]$, are determined by the equilibrium constant K .

$$K = [\text{A}^-][\text{B}^+]/[\text{AB}]$$

The dissociation of molecules can occur at the surface of solid particles dispersed in the solution. The examples are sialic acid groups on the surface of the blood cell (Ohshima and Kondo, 1987), carboxylic acid or sulfonic acid groups on synthetic latex particles (Israelachvili, 1991, p. 213), and amphoteric hydroxyl groups on oxide surfaces such as silica and metal (Hunter, 1993, p. 379). Ions can be trapped in, for instance, clay minerals, i.e., the isomorphous substitution of Si^{+4} by Al^{+3} occurs on the surface, resulting in a negative surface charge. Also, there can be differences between affinities of two phases for ions. Polarization can occur and charges can be induced. Thus, there are many causes for interfaces to be charged.

If the solid surface carries charges, an electrostatic field, E , is generated to attract counterions and to repel co-ions in the solution. Thus, a modification of the ionic distribution occurs to form an electrical double layer and gives rise to a surface potential.

10.2.1 The Poisson-Boltzmann Equation and the Debye-Hückel Approximation

In an electrolyte solution, the electrochemical potential, $\bar{\mu}_k = \mu_k + z_k e \psi$, of any ion, say, of type k , can be written, if dilute, as

$$\bar{\mu}_k = z_k e \psi + k_B T \ln c_k \quad (10.14)$$

where z_k and c_k are the valency (positive or negative) and the molar concentration of the ion of type k , respectively, and ψ is the electrostatic potential.

In equilibrium (no electric current, Exercise 10.5), the electrochemical potential, $\bar{\mu}_k$, of the k -th ions must be equal everywhere in the solution, but the electrostatic potential may be a function of position. Since the ion number density n_k is proportional to c_k , Eq. 10.14 yields the Boltzmann distribution:

$$n_k = n_k^0 \exp(-z_k e \psi / k_B T) \quad (10.15)$$

where n_k^0 is the density of the ion at the location of zero potential. According to the Poisson equation, if the dielectric constant, ϵ , does not depend on position, the potential, ψ , is related to the distribution of a net excess electric charge density, $\rho_f = \sum_k z_k e n_k$. Namely, $\epsilon_0 \epsilon \nabla^2 \psi = -\rho_f$. By using Eq. 10.15,

$$\epsilon_0 \epsilon \nabla^2 \psi = -e \sum_k z_k n_k^0 \exp(-z_k e \psi / k_B T) \quad (10.16)$$

This equation is called the Poisson-Boltzmann equation and the basis of the Gouy-Chapman model in treating the ion distribution near the surface of a foreign material in the solution.

The potential appearing in the Boltzmann equation, Eq. 10.15, and that in the Poisson equation are slightly different in the averaging processes. The potential in Eq. 10.15 is the potential of a mean force, whereas that in the Poisson equation is the local average potential. However, the difference is usually ignored.

The assumptions in deriving Eq. 10.16 are that the electrolyte is an ideal solution with uniform dielectric properties and the ions are point charges. For a discussion on the limitation of the applicability of this equation see Hunter (1981). The Poisson-Boltzmann equation seems to be very accurate if the electrolyte concentrations do not exceed 1 M and the surface potential is less than 200 mV. However, the equation does not take into consideration the attractive van der Waals forces among ions. They seem to be important when ionic distances are small (< 4 nm) (Guldbrand et al., 1984; Kjellander et al., 1988, 1990). The finite size of ions tends to enhance the repulsion between two surfaces. The image forces may contribute additional repulsion between surfaces. Surface charges are discrete and the discreteness may introduce an attractive force if the surface charges are mobile.

The Poisson-Boltzmann equation determines the potential as well as n_k . Consider an ion with charge $z_k e$ in the solution which is isotropic around the ion. The potential microscopically varies violently from point to point near other ions, but we take the spatially averaged potential, ψ , which is then spherically symmetric around the charge $z_k e$. Assuming that the electric energy, $z_k e \psi$, is small compared to thermal energy, $k_B T$, we rewrite Eq. 10.16 by expansion as

$$\nabla^2 \psi = -(1/\epsilon_0 \epsilon) \left[\sum_k z_k e n_k^0 - \sum_k z_k^2 e^2 n_k^0 \psi / k_B T \right] \quad (10.17)$$

The first summation term must be zero to preserve electroneutrality in the bulk solution, so that

$$\nabla^2 \psi = \kappa^2 \psi, \quad (10.18)$$

where

$$\kappa = \left(e^2 \sum_k z_k^2 n_k^0 / \epsilon_0 \epsilon k_B T \right)^{1/2} \quad (10.19)$$

The above assumption for the simplification is called the Debye-Hückel approximation. The quantity κ is called the Debye-Hückel screening parameter. (From Exercise 10.7, $1/\kappa = 9.6$ nm for 10^{-3} M 1:1 aqueous electrolyte at 25°C .)

If Eq. 10.18 is solved around an ion with a charge $z_k e$, and if the total charge in the system as a whole vanishes, the potential decays exponentially as

$$\psi(r) = \frac{z_k e}{4\pi\epsilon_0\epsilon} \frac{1}{(1 + \kappa a)r} e^{-\kappa(r-a)}, \quad (r > a) \quad (10.20)$$

assuming no specific adsorption in the very thin Stern layer. Here, the ion is assumed to be a sphere of radius a . The factor, $(1 + \kappa a)$, guarantees the electroneutrality because the total charge in the double layer:

$$4\pi \int_a^\infty \rho_f r^2 dr = -4\pi\epsilon_0\epsilon \int_a^\infty (\nabla^2 \psi) r^2 dr = -z_k e, \quad (\nabla^2 \psi = \kappa^2 \psi)$$

This potential is known to be a good approximation to the exact solution of the Poisson-Boltzmann equation for small κa (MacGillivray, 1969).

The solution of Eq. 10.18 may be used in Eq. 10.15 to find the ionic distribution.

10.2.2 The Electric Double Layer

The surface of a solid (metal or mercury) immersed in an electrolyte solution is usually electrically charged, as discussed at the beginning of Sec. 10.2. The surface charge density can be large and the condition of the Debye-Hückel approximation does not hold in most cases in the vicinity. We must then use Eq. 10.16 without approximations there. For simplicity, we consider that the surface is flat and $z_k = z_+ = -z_- \equiv z$, so that the electrolyte is symmetric $z:z$. By choosing the x coordinate perpendicularly away from the flat surface we have

$$\frac{d^2\psi}{dx^2} = \frac{2n^0ze}{\epsilon_0\epsilon} \sinh \frac{ze\psi}{k_B T} \quad (10.21)$$

For a unique solution of this equation we set the boundary conditions. In the bulk solution ($x \rightarrow \infty$), the excess charge vanishes and the electroneutrality holds, where we define both ψ and $d\psi/dx$ as null. Near the solid surface, other types of forces, such as van der Waals' interactions, can be important between ions and the surface, or the ionic size must be considered, or the dielectric constant may be different from the bulk value. The Poisson-Boltzmann equation, Eq. 10.16, cannot be used there and we must separately treat this region ($0 < x < d$) which is about an ionic radius away from the surface (Exercise 10.9). Therefore, we set another boundary plane at $x=d$ in the double layer, and denote by ψ_d the potential on the plane.

Now, multiplying both sides of Eq. 10.21 by $2(d\psi/dx)$ and noting that $2(d\psi/dx)(d^2\psi/dx^2) = d/dx(d\psi/dx)^2$, we integrate with respect to x from some point out in the bulk solution ($x \rightarrow \infty$) up to some point near the surface ($x=d$). Then, since $\cosh y - 1 = \frac{1}{2}(e^y + e^{-y} - 2) = \frac{1}{2}(e^{y/2} - e^{-y/2})^2 = 2 \sinh^2(y/2)$, we have

$$\frac{d\psi}{dx} = - \frac{2\kappa k_B T}{ze} \sinh \frac{ze\psi}{2k_B T} \quad (10.22)$$

where κ is the Debye-Hückel parameter (Eq. 10.19). Note that on the way of calculation we have $(d\psi/dx)^2$. On taking the square root of this quantity we will have the double sign \pm , but we choose the negative sign, as appearing in Eq. 10.22. This is because $d\psi/dx$ must be negative for $\psi > 0$ and positive for $\psi < 0$, so that $|\psi|$ decreases as going away from the flat surface.

In order to find ψ , Eq. 10.22 is integrated once more with respect to x from an infinity to the plane at $x=d$, where the Gouy-Chapman theory is considered to be applicable. Writing $y \equiv ze\psi/k_B T$ and $u \equiv e^{-y/2}$, Eq. 10.22 leads to

$$\frac{dy}{dx} = - \frac{2}{u} \frac{du}{dx} = \kappa \left(e^{-\frac{y}{2}} - e^{\frac{y}{2}} \right) = \kappa \frac{u^2 - 1}{u}$$

Therefore, by integrating

$$\kappa x + \text{const} = \ln \frac{1+u}{1-u}$$

where the integration constant is determined by the potential ψ_d at $x=d$. Since $(u-1)/(u+1) = \tanh(y/4)$, we have, for $x > d$,

$$\tanh(ze\psi/4k_B T) = \tanh(ze\psi_d/4k_B T) \exp[-\kappa(x-d)] \quad (10.23)$$

For very low potentials, this agrees with the solution obtained under the Debye-Hückel approximation (Eq. 10.18 and Exercise 10.13).

The total charge, per unit area of surface, in the diffuse layer is given by

$$\sigma_d = \int_d^{\infty} \rho_f dx = - \int_d^{\infty} \epsilon_0 \epsilon \frac{d^2 \psi}{dx^2} dx \quad (10.24)$$

Since $d\psi/dx$ must vanish as $x \rightarrow \infty$, we have

$$\sigma_d = \epsilon_0 \epsilon \left(\frac{d\psi}{dx} \right)_{x=d} \quad (10.25)$$

Here we may use Eq. 10.22 to express σ_d in terms of ψ_d and obtain

$$\sigma_d = - \frac{2\kappa k_B T \epsilon_0 \epsilon}{ze} \sinh \frac{ze\psi_d}{2k_B T} \quad (10.26)$$

If there are no ions because of their finite size within $x < d$, $\sigma_d = -\sigma_0$, where σ_0 is the surface charge density at $x=0$.

For very low potential, from Eq. 10.26

$$\sigma_d = -\epsilon_0 \epsilon \kappa \psi_d \quad \text{or} \quad \psi_d = -\sigma_d / \epsilon_0 \epsilon \kappa \quad (10.27)$$

This is a relation for a capacitor with a parallel-plate capacitance, $C_d^i = \epsilon_0 \epsilon \kappa$. The quantity, C_d^i , is called the integral capacitance of the (diffuse) double layer.

In general, the differential capacitance of the diffuse double layer, C_d , is defined by

$$C_d = - \frac{d\sigma_d}{d\psi_d} = \epsilon_0 \epsilon \kappa \cosh \frac{ze\psi_d}{2k_B T} \quad (10.28)$$

For $\psi_d \ll 2k_B T/ze$, this capacitance is reduced to the above linear case of $\epsilon_0 \epsilon \kappa$. The observed capacitances are always much less than the theoretical capacitance given by Eq. 10.28, indicating the importance of the region, $0 < x < d$.

10.2.3 Stern Layer or the Compact Layer

The above analysis clearly breaks down at very short distances from the particle surface ($0 < x < d$). This is not only because of the finite size of the ions but also due to the possibility that the dielectric constant of the solution near the surface differs from the bulk value (Exercise 10.14). Another important reason is that ions have, in addition to the electric forces among charges, other interactions with solid surfaces, like van der Waals' forces, which can be large at short distances and are not included in the Poisson-Boltzmann equation.

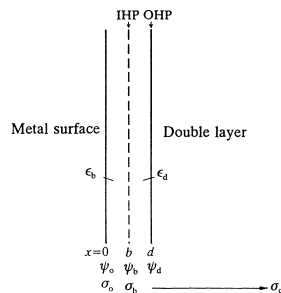


Fig. 10.1 The Stern layer as modified by Grahame.

The detailed behavior of the electrolyte solution near the surface may be investigated by determining the surface tension as a function of applied potential by using an electrocapillarmeter (Sec. 10.2.4). This apparatus uses mercury as an electrode, but the information obtained can, in some cases, be extended to the solid-solution interfaces.

Stern treated the region near the surface separately from the region of the so-called double layer (Sec. 10.2.2). This region is called the Stern or compact layer. Stern loosely considered this layer to be bounded by a plane at $x=d$, where the model of the double layer ceases to hold. This boundary plane is called the Stern plane. The Stern model (Fig. 10.1) was refined by Grahame (1947).

For simplicity, we consider, again, an electrolyte of one type ($z:z$). In the Grahame model of the compact layer, ions are considered to have finite sizes and there is a plane of closest approach at $x=b$. This plane may or may not lie inside the compact layer. Unless it is inside the compact layer ($b \leq d$), no ions can exist inside the compact layer. If so, there is no charge in the layer and the potential changes linearly with x in the region, $0 < x < d$. If not, the well-known Langmuir adsorption occurs on this plane at $x=b$. (Such absorption inside the compact layer is called the specific adsorption.) We denote by n_b and N_b the surface number density of adsorbed ions and the maximum possible surface number density of occupiable sites on this plane, respectively. The rate of the adsorption of ions on the plane per unit time can be written as $k^+(N_b - n_b)n$, where k^+ is the rate constant and n is the number density of the ion in the bulk. The rate for the adsorbed ions to leave the plane per unit time is k^-n_b with the rate constant k^- . (Later, assuming that the solution is dilute, n is replaced by the mole fraction so that k^+ and k^- have the same dimension.) In equilibrium, these rates must be equal. Therefore, the charge due to the specific adsorption on the plane b is given by

$$\sigma_b = zen_b = zeN_b \frac{Kn}{1 + Kn} \quad (10.29)$$

where $K = k^+/k^-$ is the equilibrium constant. The constant K is dimensionless if n is expressed in the mole fraction and K can be written as follows:

$$K = \exp[-(ze\psi_b + \phi)/k_B T] \quad (10.30)$$

where ψ_b is the potential at the plane of the closest approach and ϕ is the specific chemical adsorption potential of the ions. These ions may be counterions but can be co-ions (the same ions as on the surface) if they are of small size and van der Waals' interactions with the solid surface are large.

Some ions, in particular, hydrated cations, can never get closer to a mercury or metallic surface than the distance of d and cannot be specifically adsorbed within the compact layer because of their larger size due to hydration. Their adsorption can be described purely by their electrical response in the diffuse part of the double layer. Examples are small positive ions, like Li^+ , Na^+ , and K^+ , which have a strong affinity to water molecules and are strongly hydrated to form large ions and remain hydrated when approaching the solid surfaces (Israelachvili, 1991, p. 55). In contrast, monovalent anions, like halide ions (Cl^- , Br^- , I^-) are only weakly hydrated and can easily release water molecules to penetrate into the inner region. The locus of the center of these anions is called the inner Helmholtz plane at $x=b$. Thus, they are *specifically adsorbed* on the inner Helmholtz plane (IHP). But not all anions are able to do this. The example is F^- at least at modest concentrations (Payne, 1972). On the other hand, the plane at which the diffuse layer initiates is called the outer Helmholtz plane (OHP), which will coincide with the Stern plane.

A thermodynamical approach to the problem of detecting specific adsorption has been discussed by Hall (1980) and Hall and Rendall (1980). It is independent of the Grahame model of the double layer, but uses the ζ -potential (Sec. 10.5.1).

Since $\sigma_b = ze n_b$ in the Grahame model, where n_b and σ_b are the surface number density of the ions and the ionic surface charge density, respectively. If σ_0 designates the charge density on the solid surface, from the electroneutrality as a whole we have

$$\sigma_0 = \sigma_b + \sigma_d \quad (10.31)$$

where σ_d is the ionic charge in the double layer per unit area, Eq. 10.26. The regions, $0 < x < b$ and $b < x < d$, are assumed to be free of charge. The dielectric constants for these regions may be denoted by ϵ_b and ϵ_d , respectively. Then (see Fig. 10.2)

$$\psi_0 - \psi_b = \sigma_0 b / \epsilon_0 \epsilon_b \quad \text{and} \quad \psi_b - \psi_d = -\sigma_d (d - b) / \epsilon_0 \epsilon_d \quad (10.32)$$

Here, $\epsilon_0 \epsilon_b / b = C_b^G$ and $\epsilon_0 \epsilon_d / (d - b) = C_d^G$ are the respective capacitances for these regions in the Grahame model.

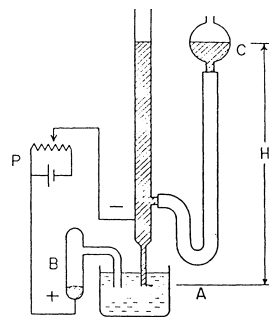
The above model has been experimentally examined by Buff and Goel (1969), Levine (1971), and Robinson and Levine (1973).

If there is no specific adsorption, $\sigma_b = 0$ and $\sigma_d = -\sigma_0$. We then write

$$\frac{\psi_0 - \psi_d}{\sigma_0} = \frac{1}{C_T} = \frac{1}{C_b^G} + \frac{1}{C_d^G} \quad (10.33)$$

Grahame's observation (1947) by using the electrocapillarometer with NaF as an electrolyte shows that C_b^G is not constant but depends on the charge on the metal

Fig. 10.2 Sketch of the electrocapillarometer. A: Capillary tip, B: Reference electrode, C: Mercury pool, P: Potentiometer, H : Height of mercury column, (Usui, 1984, with permission from Marcel Dekker).



surface. If C_d^G is large in Eq. 10.33, it can be ignored compared to C_b^G in determining C_T . Therefore, C_b^G can be measured if high electrolyte concentration (~ 1 M) is used as suggested by C_d^i of Eq. 10.27. Assuming that $b \sim 0.5$ nm, Payne (1972) obtained that $\epsilon_b = 18$ compared to the normal value of 80 for bulk water. This is possible because the orientation of water molecules is not partially free near the mercury surface.

10.2.4 Electrocapillarometer

It has long been known that the form of a curved surface of mercury in contact with an electrolyte solution depends on its state of electrification because of a change of the surface tension. The earliest investigation of the electrocapillary effect was made by Lippmann (1875). Fig. 10.2 is a sketch of an electrocapillarometer, which uses mercury as an electrode material. The height of the mercury column H gives the surface tension γ :

$$\gamma = (1/2)R\rho gH \quad (10.34)$$

provided the solution wet the capillary, where R is the radius of the capillary, ρ is the density of mercury, g is the gravitational acceleration.

Consider that the mercury-solution interface is electrified, carrying a surface charge density, σ_0 . If the interface is at a potential, ψ_0 , then, by using Eq. 10.1, we find that the surface electrostatic energy density is given by $\sigma_0\psi_0$ (Exercise 10.14). This energy must be added as an additional surface energy to Eq. 2.15 of Chapt. 2. The best procedure, however, is to use the electrochemical potential of Eq. 10.14, or $\bar{\mu}_k = z_k e \psi_0 + \mu_k$, since the quantity, $\bar{\mu}_k$, is now the quantity which does not depend on position, x , y , z . In treating the mercury-solution interface we use the Gibbs concept of a dividing surface (Sec. 2.1.1) and introduce a surface concentration, Γ_k , of k -th ions. We have

$$\sigma_0 = \sum_k \Gamma_k z_k e \quad (10.35)$$

where the summation must include the free electrons of mercury and mercury ions (the valency, z_e , of free electrons, $z_e = -1$). Now, if the potential is changed by $d\psi_0$, Gibbs adsorption isotherm, Eq. 2.25, is affected only by ions and free electrons and we have

$$-d\gamma = \sum_k \Gamma_k d\bar{\mu}_k$$

Therefore, we obtain the Lippmann relation:

$$\left(\frac{d\gamma}{d\psi_0} \right)_{[\mu], T, p} = -\sigma_0 \quad (10.36)$$

(See Usui (1984) for the more detailed derivation.) Note that the Volta potential and the potential jump at the interface due to oriented dipoles can be considered as constant and these values do not affect the Lippmann equation.

From Eq. 10.36, we find that the surface charge density vanishes, when the interfacial tension is maximum relative to the variation of the applied potential. If the applied potential is different from that for the zero charge, Eq. 10.36 may be used to determine the surface charge density by means of an electrocapillarmeter. The direct measurement can be made by raising the head of the mercury column, so that a steady stream of mercury droplets occurs. The falling droplets carry the surface charges with them to the bottom, where another mercury electrode is present, so that an electric current can be observed. It may be assumed that the mercury drops are spherical and the radius is the same as that of the glass capillary, so that the charge carried by each drop is $4\pi R\sigma_0$. The falling rate of the droplets accordingly determines the value of σ_0 .

10.2.5 Test of the Poisson-Boltzmann Equation

The core of the Gouy-Chapman model of double layers is based on the Poisson-Boltzmann equation. Theoretically, Monte-Carlo simulations of Torrie and Valleau (1979) and Jonsson et al. (1980) seem to confirm the validity of the Poisson-Boltzmann equation down to length scales of a few nanometers, ignoring the Stern layer. An important thing is, however, the applicability of the theory to a real system.

The presence of the double layer in the electrolyte solution intervening charged solid surfaces introduces, as discussed in the following section, electrostatic forces due to the electric stress discussed in Sec. 10.1. The real test may be made by measuring this force, which is described in the next section.

The force between surfaces immersed in an ionic solution consists of attractive van der Waals and repulsive (electrostatic) forces. Israelachvili and Adams (1978) used an improved technique of measuring forces directly down to 0.1 nm in aqueous solutions with molecularly smooth mica surfaces. Their experiments were

conducted at the surface potential of about -130 mV at infinite separation. Their results agree very well with theoretical calculations based on the Gouy-Chapman model down to separations of about 10 nm in 10^{-4} M KNO_3 solution ($1/\kappa \sim 29$ nm). Pashley and Israelachvili (1984) show a good agreement with the Gouy-Chapman theory of divalent ions corrected for the van der Waals attractions with a Hamaker constant of $2.2 \cdot 10^{-20}$ J (Eq. 10.43). Thus, there are unambiguous evidences that the model accurately describes the electrostatic interactions between charged surfaces, except for small distances.

10.3 Interacting Planar Double Layers

The interaction energy between two charged particles depends on the distance of separation. If the Poisson-Boltzmann equation, Eq. 10.16, holds irrespective of the presence of the second body at any distance, the surface potential, ψ_0 , will remain constant on its approach (constant surface potential conditions). However, a question arises as to the surface charge, which is regulated by surface ionization under the mass action equilibria (Chan et al., 1976, 1980). If the counterions diffuse rapidly to the surfaces, while they approach close to one another, the equilibria are attained and the surface charge density, σ_0 , will remain constant (constant surface density conditions). The constant charge conditions give a slightly higher value for the repulsive force, in particular, when the separation is small and the surface potential (measured when infinitely separated) is small. In general, however, the real interaction energy will lie between the two limits (see Israelachvili and Adams (1978) and Pashley and Israelachvili (1984)).

10.3.1 Symmetric Case

Suppose that two parallel similar plates are immersed in a solution of a symmetrical electrolyte, separated by a distance H . The double layers at each plate then overlap each other. An electric stress, given by $\frac{1}{2}\epsilon_0\epsilon E^2$ (Eq. 10.13), will appear in the solution. On the other hand, the ionic distribution introduces an osmotic pressure. The total pressure due to the separation of ions in the solution is the sum of these two. If the system is in equilibrium this sum must be constant everywhere and can be evaluated anywhere inside the solution.

We assume that the Poisson-Boltzmann equation, Eq. 10.21, holds with boundary conditions:

$$\text{At } x = H/2, \quad \psi = \psi_{H/2} \quad \text{and} \quad d\psi/dx = 0$$

$$\text{At } x = 0, H, \quad \psi = \psi_0$$

Integrating Eq. 10.21 once (noting different boundary conditions from those for Eq. 10.22), we have

$$2n^0 k_B T \cosh \frac{ze\psi}{k_B T} - \frac{1}{2} \epsilon_0 \epsilon \left(\frac{d\psi}{dx} \right)^2 = \text{a constant} \quad (10.37)$$

We identify that the second term is the electric stress of Eq. 10.13. Since the sum of this stress and the osmotic pressure is a total pressure, which is constant, the above equation, Eq. 10.37, suggests that the first term is related with the osmotic pressure. This assertion can be shown to be true as follows.

The osmotic pressure can be found by the van't Hoff equation under ideal-solution approximations:

$$\Pi = nk_B T \quad (10.38)$$

where n is the excess ions per unit volume. In the present case, the excess ion density is given by

$$n = n^0 [\exp(-ze\psi/k_B T) - 1 + \exp(-ze\psi/k_B T) - 1]$$

By assumption, the present electrolyte is symmetrical ($z:z$) and, therefore,

$$\Pi = 2n^0 k_B T \left[\cosh \frac{ze\psi}{k_B T} - 1 \right] \quad (10.39)$$

Now, we note that the electric field, $-d\psi/dx$, at the central plane at $x=H/2$ must vanish from the symmetry, yielding that the total pressure at this central plane is due to the osmotic pressure alone. The total pressure p_T in the solution is, therefore, given by

$$p_T = 2n^0 k_B T \left[\cosh \frac{ze\psi_{H/2}}{k_B T} - 1 \right] \quad (10.40)$$

This is the repulsive force, F , acting on the plate per unit area.

The repulsive force vanishes as $H \rightarrow \infty$. The repulsive potential energy or the repulsive free energy of the plates at the distance of separation of H is given by the work required to bring them to this distance:

$$\Delta G_R = - \int_{\infty}^H p_T dH \quad (10.41)$$

Here, the suffix "R" of ΔG_R stands for the repulsive part. For very low potentials at $x=H/2$, the cosh term in Eq. 10.40 can be expanded. If the potentials at x

$=H/2 \gg d$ is approximated by adding the potentials due to each plane (Eq. 10.23 with $d \sim 0$), we obtain

$$\psi_{H/2} = 2\psi(x = H/2) = \frac{8k_B T}{ze} \tanh \frac{ze\psi_0}{4k_B T} e^{-\kappa \frac{H}{2}}$$

Here, we have simplified Eq. 10.23 for small ψ by expansion on the left-hand side. Finally, we find

$$\Delta G_R = \frac{64n^0 k_B T}{\kappa} \tanh^2 \frac{ze\psi_0}{4k_B T} e^{-\kappa H} \quad (10.42)$$

The repulsive force is given by $-\mathrm{d}\Delta G_R/\mathrm{d}H$. This force agrees with Eq. 10.40 under the approximation used.

Equation 10.42 holds for large κH (at least >2). For small ψ_0 , we can use the Debye-Hückel approximation to obtain $\psi_{H/2}$ and find the repulsive force given in Exercise 10.21. This result suggests that a better approximation to Eq. 10.42 may be obtained by dividing it by $(1+e^{-\kappa H})$.

If we impose the condition ψ_0 is constant, $(\mathrm{d}\psi/\mathrm{d}x)_{x=0}$ becomes smaller as H decreases. This is because the two overlapping double layers have opposite slopes and their overlapping increases as H decreases. Since the surface charge density σ_0 is related with the potential gradient at a conducting surface ($\sigma_0 = -\epsilon_0 \epsilon (\mathrm{d}\psi/\mathrm{d}x)_{x=0}$), the surface charge decreases as H decreases. However, we can consider another extreme case of the constant charge densities. If σ_0 , rather than ψ_0 , on each plate is constant, the repulsive force per unit area between them can also be obtained in the similar way (Exercise 10.22).

We must note that the above interactions between the plates do not include the attractive van der Waals interaction. This energy per unit area is given by

$$\Delta G_A = -\frac{A}{12\pi H^2} \quad (10.43)$$

where the suffix “A” of ΔG_A stands for the attractive part and A in the numerator is the Hamaker constant (see Chapt. 8). The attractive force is given by $-\mathrm{d}\Delta G_A/\mathrm{d}H$.

Thus, the total potential energy of interaction between surfaces seems to be the sum, $\Delta G_R + \Delta G_A$. However, many experiments indicate that there is a need of an extra term ΔG_S . The total interaction free energy is, therefore, written as

$$\Delta G_T = \Delta G_A + \Delta G_R + \Delta G_S \quad (10.44)$$

The last term is called the solvent-structural term due to repulsive and attractive solvent mediated forces. These forces are important at small separation of up to about 5 nm. At present, however, it is not well understood because of the lack of

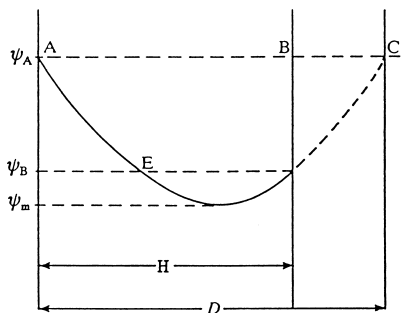


Fig. 10.3 The potential distribution for two plates at potentials, ψ_A and ψ_B , respectively (Hunter, 1993, with permission from Oxford University Press).

an adequate theory for the structure of water related hydration forces and hydrophobic forces.

10.3.2 Flat Particles with Dissimilar Double Layers

Many sols of practical interest contain more than one type of particles, so that it may be useful to consider the mutual interaction of dissimilar double layers. In Fig. 10.3, A and B designate the flat surfaces at $x=0$ and H , respectively. The boundary conditions are given by

$$\begin{aligned} x = 0, \quad \psi &= \psi_A \\ x = H, \quad \psi &= \psi_B < \psi_A \end{aligned} \quad (10.45)$$

The governing equation is Eq. 10.37 and the solution, ψ , for the present case must coincide partly with that of the symmetric case ($\psi_A = \psi_B = \psi_0$, Sec. 10.3.1) as seen in Fig. 10.3. Therefore, the force acting on the plate must be the same as the symmetric case.

In the present case, ψ_A , ψ_B , and H are shown in Fig. 10.3. The distance H , corresponding to the separation of the symmetric case, is determined by adjusting the position of the plate C as shown in Fig. 10.3, so that the potential curve passes through ψ_B and ψ_C . Then, the potential at $x=H/2$ gives the pressure on the plates by Eq. 10.40. We must find this potential.

The potential, $\psi(x)$, can be obtained by solving Eq. 10.37, possibly, under the Debye-Hückel approximation. Namely, Eq. 10.18 is solved for the present case under the boundary conditions Eq. 10.45. The result is given by

$$\psi(x) = \psi_A \cosh \kappa x + \left(\frac{\psi_B - \psi_A \cosh \kappa H}{\sinh \kappa H} \right) \sinh \kappa x \quad (10.46)$$

Using this equation, charge densities on the plates can be found (Exercise 10.24).

The total potential energy of repulsion between the plates, A and B, can be obtained by noting that the two parts, x in $(0, D/2)$ and x in $(D/2, H)$, can be treated separately. Thus,

$$\Delta G_R(AB) = \frac{1}{2} \Delta G_R(AC) + \frac{1}{2} \Delta G_R(EB) \quad (10.47)$$

the two terms on the right-hand side are symmetric cases (Eq. 10.42). The value of D can be found from Eq. 10.46, since $\psi(x=D) = \psi_A$ (Exercise 10.26).

The potential of repulsion per unit area, Eq. 10.47, can also be found by the free energy, $\Delta G_R(H) = \Delta G(H) - \Delta G(\infty)$, where the free energy involved in establishing a double layer A is given by $-\frac{1}{2} \sigma_A \psi_A$ and $\Delta G(H)$ is the sum of those for double layers, A and B. Hogg et al. (1966) used this method to obtain

$$\Delta G_R = \frac{\epsilon_0 \epsilon \kappa}{2} [\pm (\psi_A^2 + \psi_B^2)(1 - \coth \kappa H) + 2\psi_A \psi_B \operatorname{cosech} \kappa H] \quad (10.48)$$

Choose “+” in the double sign when ψ_A and ψ_B are kept constant while the surfaces approach. From this result the interaction force can be obtained (Exercise 10.25). The behavior of this force is complicated with respect to the distance. For instance, the force can change from “repulsive” to “attractive” at a certain distance when the surfaces approach each other if the potentials have the same sign but different magnitudes.

In Eq. 10.48, the “-” sign stands for the case when surface charges are kept constant rather than the potentials while the surfaces approach each other.

10.4 Interaction between Charged Spheres

In many disperse systems, dispersed particles are better represented by a spherical model, rather than by plane parallel plates. The double layers may also be treated in terms of the Poisson-Boltzmann equation in a spherical case, but mathematically more complex.

Honig and Mul (1971) commented on various theoretical results appeared in the literature on this subject before 1969.

10.4.1 For Large Values of κa (~ 2.5)

It is often the case that two bodies do not interact significantly unless the distance of the closest approach is smaller than the radii a of curvature of the bodies. This condition corresponds to that $1/\kappa \ll a$ in the present case.

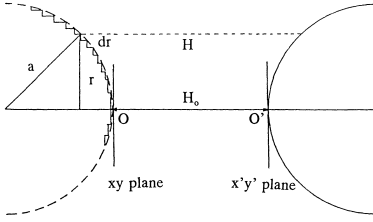


Fig. 10.4 Geometry of calculating the interaction of two spheres.

Consider that two identical spheres of radius a approach each other under a constant potential, ψ_0 . They are considered to have stepped surfaces (Fig. 10.4), which form a parallel ring of area $2\pi r dr$ on each sphere. The parallel rings interact each other as if they are flat plates. The total energy of repulsion is then obtained by integration for spheres at a distance H_0 .

$$\Delta G_R^{\text{sphere}}(H_0) = 2\pi \int_0^\infty \Delta G_R^{\text{plane}}(H) r dr \quad (10.49)$$

Here we assume that the separation is small compared with the radius, so that the important contribution to the repulsion comes from small values of r and the upper limit of integration is extended to ∞ (if $\kappa a > 2.5$). From Fig. 10.4,

$$\frac{1}{2}(H - H_0) = a - (a^2 - r^2)^{1/2} \quad (10.50)$$

By differentiation,

$$2r dr = (a^2 - r^2)^{1/2} dH \sim a dH \quad (a \gg r) \quad (10.51)$$

Therefore,

$$\Delta G_R^{\text{sphere}}(H_0) = \pi a \int_{H_0}^\infty \Delta G_R^{\text{plane}}(H) dH \quad (10.52)$$

This equation gives the Derjaguin method of calculating the interaction between two spheres from the interaction of two parallel plates per unit area (Derjaguin, 1934). Substitution of Eq. 10.42 into $\Delta G_R^{\text{plane}}$ of Eq. 10.52 we obtain

$$\Delta G_R(H_0) = \frac{64n^0 k_B T}{\kappa^2} \pi a \gamma^2 e^{-\kappa H_0} = \frac{16\epsilon_0 \epsilon k_B^2 T^2}{n^0 z^2 e^2} \pi a \gamma^2 e^{-\kappa H_0} \quad (10.53)$$

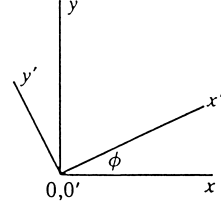


Fig. 10.5 Definition of ϕ . See Fig. 10.4 for x , y , x' , and y' ($\phi=0$ if $x \parallel x'$).

where $\gamma = \tanh(ze\psi_0/4k_B T)$. As a special case, for very low ψ_0 , we use the Debye-Hückel approximation and obtain the following, by substituting the result of Exercise 10.20 into $\Delta G_R^{\text{plane}}$,

$$\Delta G_R(H_0) = 2\pi a \epsilon_0 \epsilon \psi_0^2 \ln[1 + e^{-\kappa H_0}] \quad (10.54)$$

If the surface charge density, rather than ψ_0 , is constant, Exercise 10.21 may be used.

Chan and Chan (1983) numerically solved the Poisson-Boltzmann equation and showed that the Derjaguin method produced very accurate results for constant potential boundary conditions for thin double layers ($\kappa a > 10$).

White (1983) considered a general case of two interacting solid particles, 1 and 2. If the particle 1 has the radii of curvature of a_1 and a'_1 at the surface facing the particle 2 which has the radii of curvature, a_2 and a'_2 . We denote by ϕ the relative angle between a_1 and a_2 (Fig. 10.5). Equation 10.52 should then read as, provided H_0 is small compared to the radii of curvature,

$$\Delta G_R^{\text{sphere}}(H_0) = \frac{2\pi}{\sqrt{\lambda}} \int_{H_0}^{\infty} \Delta G_R^{\text{plane}}(H) dH \quad (10.55)$$

with

$$\lambda = \left(\frac{1}{a_1} + \frac{1}{a'_1} \right) \left(\frac{1}{a_2} + \frac{1}{a'_2} \right) + \sin^2 \phi \left(\frac{1}{a_1} - \frac{1}{a_2} \right) \left(\frac{1}{a'_1} - \frac{1}{a'_2} \right)$$

If $H_0 \ll a_1, a'_1, a_2, a'_2$, Eq. 10.55 can be used for any kind of interaction energy, including the van der Waals energy. For two spheres of radii, $a_1 = a'_1$ and $a_2 = a'_2$. We then have

$$\Delta G_R(H_0) = \frac{64n^0 k_B T}{\kappa^2} \pi \frac{a_1 a_2}{a_1 + a_2} \gamma^2 e^{-\kappa H_0} \quad (10.56)$$

For attractive van der Waals energy,

$$\Delta G_A(H_0) = - \frac{2a_1 a_2}{a_1 + a_2} \frac{A}{12H_0} \quad (10.57)$$

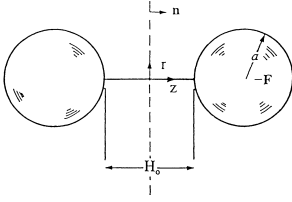


Fig. 10.6 Geometry of two spheres (Russel et al., 1989, with permission from Cambridge University Press).

A more accurate ΔG_R can be obtained by numerically integrating Eq. 10.52 in terms of the exact value of $\Delta G_R^{\text{plane}}$ at each separation. On the other hand, Glendinning and Russel (1983) and Russel et al. (1989) used the method described in Sec. 10.3.1. Namely, the repulsive force F is obtained by integrating the total pressure over the central plane between the two spheres under the equilibrium condition. The total pressure is given by the osmotic pressure, Eq. 10.40, and electrostatic stress, Eq. 10.12. Therefore,

$$\mathbf{F} = \int_S (2n^0 k_B T \left[\cosh \frac{ze\psi_S}{k_B T} - 1 \right] \mathbf{n} + \epsilon_0 \epsilon \left[\mathbf{E}\mathbf{E} - \frac{1}{2} \mathbf{E} \cdot \mathbf{E} \mathbf{\hat{I}} \right] \cdot \mathbf{n}) dS \quad (10.58)$$

where ψ_S is the potential on the central plane. For a symmetrical $z:z$ electrolyte solution, the Poisson-Boltzmann equation, Eq. 10.17 reads as

$$\nabla^2 \Psi = \kappa^2 \sinh \Psi, \quad \Psi = ze\psi/k_B T \quad (10.59)$$

Choose cylindrical coordinates (r, ϕ, z) with the origin at the center between the two spheres and the z axis along the line joining the centers of the spheres (Fig. 10.6). By scaling for thin double layers, i.e. $\kappa a \gg 1$, new variables are defined by

$$z' = \kappa z \quad \text{and} \quad r' = (\kappa a)^{1/2} r/a \quad (10.60)$$

There is no ϕ -dependence from symmetry. Equation 10.59 reads now

$$\frac{\partial^2 \Psi}{\partial z'^2} - \sinh \Psi = \frac{1}{\kappa a} \frac{1}{r'} \frac{\partial}{\partial r'} r' \frac{\partial \Psi}{\partial r'} \quad (10.61)$$

We expand the potential as

$$\Psi = \Psi_1(r', z') + (\kappa a)^{-1} \Psi_2(r', z') + \dots \quad (10.62)$$

From Fig. 10.6 the equation of the spherical surface is given by $z = (H_0/2) + a[1 - \{1 - (r/a)^2\}^{1/2}]$. It is expressed, in the new variables, by

$$z' = g(r') = \frac{\kappa H_0}{2} + \kappa a \left[1 - \left(1 - \frac{r'^2}{\kappa a} \right)^{1/2} \right] \quad (10.63)$$

Thus, for large κa we are to solve

$$\frac{\partial^2 \Psi_1}{\partial z'^2} = \sinh \Psi_1 \quad (10.64)$$

with

$$\frac{\partial \Psi_1}{\partial z'} = 0 \quad \text{at} \quad z' = 0 \quad (10.65)$$

The boundary conditions are such that, on the surface of the sphere ($z' = g'(r') = \frac{1}{2}\kappa H_0 + \frac{1}{2}r'^2$),

$$\Psi_1 = \Psi_0, \quad \text{if } \psi_0 \text{ is constant,} \quad (10.66)$$

or

$$\frac{\partial \Psi_1}{\partial z'} = \frac{ze}{\epsilon_0 \epsilon k_B T \kappa} \sigma_0 \equiv q, \quad \text{if } \sigma_0 \text{ is constant} \quad (10.67)$$

The last expression is obtained as follows. If the surface charge density σ_0 is constant, $n_r \partial \psi / \partial r + n_z \partial \psi / \partial z = -\sigma_0 / \epsilon_0 \epsilon$, where (n_r, n_z) is the outward unit normal to the spherical surface. In the new variables this condition leads to Eq. 10.67 for large κa .

In order to simplify the analysis, we assume that potentials are small. The force is then given by Eq. 10.58 and, in the present approximation,

$$F_1 \approx \pi \epsilon_0 \epsilon \left(\frac{k_B T}{ze} \right)^2 \int_0^\infty \left[\kappa a \Psi_1^2 + \left(\frac{\partial \Psi_1}{\partial r'} \right)^2 \right] r' dr' \quad (10.68)$$

Therefore, we have

$$\text{Constant potential: } F_1 = 2\pi \epsilon_0 \epsilon a \kappa \psi_0^2 \frac{e^{-\kappa H_0}}{1 + e^{-\kappa H_0}} \quad (10.69)$$

$$\text{Constant charge: } F_1 = 2\pi \frac{a}{\epsilon_0 \epsilon \kappa} \sigma_0^2 \frac{e^{-\kappa H_0}}{1 - e^{-\kappa H_0}} \quad (10.70)$$

Note that $\sigma_0 = \epsilon_0 \epsilon \kappa \psi_0$ for small surface potentials (< 25 mV). These are the same as Derjaguin results.

Glendinning and Russel (1983) extended the analysis to cover Ψ_2 in Eq. 10.59. The result for the force is

$$F = F_1 \left(1 - \frac{(\kappa a)^{-1}}{1 \pm e^{-\kappa H_0}} \left[\frac{1}{3} \mp 1 + \frac{\kappa H_0}{2} \frac{1 + \frac{e^{-2\kappa H_0}}{3}}{1 \pm e^{-\kappa H_0}} \pm \frac{1}{6} e^{\kappa H_0} (1 \pm e^{-\kappa H_0})^2 \ln(1 \pm e^{-\kappa H_0}) \right] \right) \quad (10.71)$$

where F_1 is either Eq. 10.69 or Eq. 10.70 and the upper sign or the lower sign is used depending on either constant potential or constant charge, respectively. This result shows that the Derjaguin approximation for constant potential boundary conditions is fairly good for small κH_0 . However, for constant charge it is in a serious error when H_0 is much smaller than the Debye thickness ($1/\kappa$).

10.4.2 For Small Values of κa

If the radius of curvature of interacting two spheres is about the Debye thickness, $1/\kappa$, or smaller, any part of the spherical surface can not be approximated by a plane and Eq. 10.52 cannot be used. But we may use Eq. 10.58 following the method developed by Bell et al. (1970). The potentials, ψ_s , and the fields, \mathbf{E} , on the central plane are approximately obtained by a linear superposition of the potentials around the spheres given by Eq. 10.20. This equation may be rewritten for small κa as follows:

$$\psi(r) = \psi_0 \frac{a}{r} e^{-\kappa(r-a)} \quad (10.72)$$

where r is the distance from the center of the sphere. Then, the repulsive force and the energy of repulsion for interacting two spheres is given by

$$F = 4\pi\epsilon_0\epsilon\psi_0^2 a^2 \frac{1 + \kappa(H_0 + 2a)}{(H_0 + 2a)^2} e^{-\kappa(H_0 - a_1 - a_2)} \quad (10.73)$$

$$\Delta G_R(H_0) = \pi\epsilon_0\epsilon\psi_0^2 \frac{a^2}{H_0 + 2a} e^{-\kappa(H_0 - 2a)} \quad (10.74)$$

Equation 10.74 was obtained by Verwey and Overbeek (1948) for low surface potentials and for small κa .

10.5 Electrokinetic Phenomena

When an external electric field is applied to an electrolyte solution, a flow of ions and liquid, in particular, in the electric double layer occurs. We assume that the ionic distributions are not, however, much modified from the equilibrium by the flow. (The validity of this assumption will be discussed later.) If a charged particle is in the solution, it moves under the applied field and drags the solution around it. When a charged particle falls under gravity or is subject to a centrifugal force in an electrolyte solution, an ionic flow in the double layer around the particle is induced and creates an electric potential around it. These phenomena are called electrokinetic phenomena. Conversely, the ionic behavior on the surface of the charged particle can be investigated from these phenomena. The behavior is characterized in terms of a ζ -potential, which is directly related to the electric charge on the moving particle.

We have assumed that the medium is continuous. Under the same approximation, the governing field equations in electrokinetic phenomena are given by, in the steady state,

$$\text{Continuity: } \nabla \cdot \mathbf{v} = 0$$

$$\text{Momentum: } \rho_m \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p - \rho_f \nabla \psi + \rho_m \mathbf{g} + \eta \nabla^2 \mathbf{v}$$

$$\text{Ionic flux: } \mathbf{j}_k = n_k \mathbf{v} + b_k \{-z_k e (\nabla \psi) + (m_k - \rho_m V_k) \mathbf{g} - k_B T \nabla\} n_k$$

$$\text{Conservation of ions: } \nabla \cdot \mathbf{j}_k = 0$$

$$\text{Poisson's eq.: } \varepsilon_0 \varepsilon \nabla^2 \psi = -\rho_f$$

Boundary conditions:

$$\begin{aligned} \text{On the surface (0), } \quad \mathbf{v} &= \mathbf{v}_0, \quad (\mathbf{j}_k - n_k \mathbf{v}_0) \cdot \mathbf{n} = 0 \\ &\quad -\varepsilon_0 \varepsilon \nabla \psi \cdot \mathbf{n} = \sigma_0 \end{aligned}$$

$$\begin{aligned} \text{Far from the surface, } \quad \mathbf{v} &\rightarrow 0, \quad n_k \rightarrow \text{bulk value} \\ &\quad -\nabla \psi \rightarrow \mathbf{E}_\infty \end{aligned} \tag{10.75}$$

Here, \mathbf{v} is the fluid velocity, ρ_m is the fluid density, ρ_f is the density of free charge, \mathbf{g} is the gravity or a centrifugal acceleration, \mathbf{j}_k is the flux of the k -th ion, n_k is the number density of the k -th ion, so that $\rho_f = \sum z_k e n_k$. Other symbols, b_k , m_k , and V_k are the mobility, the mass, and the volume of the k -th ion, respectively, p is the pressure and ψ is the electrostatic potential including the external field.

The equations, Eq. 10.75, are usually solved by considering the external field, E_∞ , as a perturbation, so that every relevant quantities are expanded as a power series of E_∞ . The first terms of these expansions are, of course, the equilibrium quantities. However, we do not use this procedure here, but we try to treat the phenomena intuitively.

The measurement of ζ -potentials is important in industry. If much is not known about the dispersion, an information just on the sign, positive or negative, of the charge on a particle could be sometimes useful. With quality control, information on the value of the ζ -potentials can suggest if the product has a sufficient electrostatic repulsion to maintain its stability in the disperse system.

10.5.1 ζ (zeta)-potential

Suppose that an external electric field is applied to an electrolyte solution containing dispersed particles. Particles are usually charged and surrounded by a double layer. If they move under the field and if the particles, for instance, tend to move faster than the surrounding solution, a question arises as to how many ions in the double layer are dragged by the particles. As a simple model, a shear surface is introduced. This is a dividing surface which separates the kinetic unit (the particle plus those ions that move with it) from a medium. The potential at this surface is called the ζ -potential, ψ_ζ .

If the particle is spherical with a uniform surface charge q_0 , the shear surface is also spherical with a radius, say, a . The charge q inside this closed shear surface (including q_0) will be isotropically distributed around the surface. The ζ -potential is given by $\psi_\zeta = q_0 \exp[-\kappa(a-a_0)]/4\pi\epsilon_0\epsilon a(1+\kappa a_0) = q/4\pi\epsilon_0\epsilon a(1+\kappa a)$, with no specific adsorption (Eq. 10.20). We find that $q - q_0 \approx -O(\kappa^2 a^2)$ in the Debye-Hückel approximation.

If an electrolyte solution is in a tube, the inner wall of which is charged, the ζ -potential is given by the surface charge density, σ_ζ , inside the shear surface. Then, $\psi_\zeta = \sigma_\zeta/\epsilon_0\epsilon\kappa$ for low potentials (< 25 mV) (see Eq. 10.27).

10.5.2 Electro-osmosis and Streaming Potential

Consider a double layer at a charged solid flat surface. If an external electric field, E_∞ , is imposed parallel to the surface, the shear surface will appear just outside of the Stern layer. Ions in the double layer are exerted by electrostatic forces and the electrolyte solution is dragged by the ions parallel to the surface. Since the net charge density depends on the distance from the surface, so does the flow velocity of the solution.

If an x coordinate is chosen perpendicular to and away from the surface with $x=0$ at the shear surface, the charge density, ρ_f , in the double layer depends on x and the electric force per unit volume is given by $\rho_f E_\infty$ (Exercise 10.28). In

steady state, this must be balanced by the viscous force per unit volume, $\eta(d^2v/dx^2)$, in the solution, where η is the viscosity and v is the flow velocity.

The charge density satisfies the Poisson equation, $\epsilon_0 \epsilon d^2\psi/dx^2 = -\rho_f$. Under the Debye-Hückel approximation (Eq. 10.18), $\psi = \psi_\zeta e^{-\kappa x}$ and we have, after integration under the stick boundary conditions, $v(x=0)=0$,

$$v(x) = -(\epsilon_0 \epsilon / \eta)(1 - e^{-\kappa x})\psi_\zeta E_\infty \quad (10.76)$$

This is called the electro-osmotic flow.

This relation can be applied to an electrolyte in a tube. If E_∞ is applied, the solution in the tube has the velocity, which is proportional to the ζ -potential at the surface of the tube. If the tube is cylindrical with radius, a , the total volume, Q , of the solution flowing through the tube per unit time is

$$Q = \pi a^2 \frac{\epsilon_0 \epsilon}{\eta} \left[1 - \frac{2}{\kappa a} + 2 \frac{1 - e^{-\kappa a}}{(\kappa a)^2} \right] \psi_\zeta E_\infty \quad (10.77)$$

As $\kappa a \rightarrow 0$, $Q \rightarrow 0$. As $\kappa a \rightarrow \infty$, the flow velocity is uniform across the tube as if there are the slip boundary conditions, although Eq. 10.76 is obtained under stick boundary conditions. This implies that the region of the viscous force is confined in an infinitely thin double layer near the tube wall. The viscous force acting on the wall per unit area is easily found from Eq. 10.76. Here, the tube is assumed to be rigidly held to an external structure.

Conversely, the flow of the solution in the tube can be induced by a pressure gradient along the tube. If the viscosity is almost independent on the ionic concentration, the flow is the Poiseuille flow, given by

$$v = \frac{\Delta p}{4\eta L}(a^2 - r^2) \quad (10.78)$$

where r is the radial coordinate measured from the axis of the tube and Δp is the pressure drop along the length, L , of the tube. Since ions in the double layer near the tube wall are carried by the flow, the electric current flows. The total current is given by

$$I = 2\pi \int_0^a \rho_f(r) v(r) r dr \quad (10.79)$$

Since ρ_f does not vanish only in the region near the wall, we can simplify: $(a^2 - r^2) \approx 2a(a - r)$ in Eq. 10.78.

This current is balanced by the current due to the induced field, E . This current is approximated by

$$I' = \pi a^2 \sigma_c E \quad (10.80)$$

when the double layer contribution is small (Exercise 10.32), where σ_c is the conductivity of the solution.

Therefore, if we use the Poisson equation to rewrite ρ_f in Eq. 10.79, the field induced by the pressure gradient is given by

$$E = \frac{\varepsilon_0 \varepsilon \psi_\zeta}{\eta \sigma_c} \frac{\Delta p}{L} \quad (10.81)$$

Thus, the streaming potential difference across the tube is

$$\Delta \Psi = \frac{\varepsilon_0 \varepsilon \psi_\zeta}{\eta \sigma_c} \Delta p \quad (10.82)$$

For a more detailed derivation, see Kruyt (1952). Interestingly, Eq. 10.81 is independent of geometry. It is the same for a flow between two parallel plates, instead of in a tube.

There have been many observations of streaming potentials, including Van den Hoven and Bijsterbisch (1987). This potential difference is generally very small, unless σ_c is small, so that it is desirable to use reversible electrodes such as Ag-AgCl electrodes. The value can be used to determine the ζ -potential.

When porous plugs are present in the tube, a similar treatment can be made. See Overbeek (1952) and O'Brien and Perrins (1984).

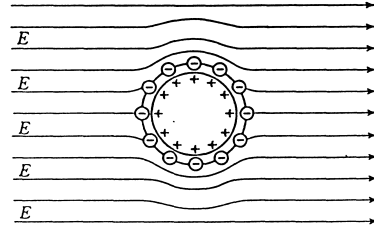
10.5.3 Electrophoresis

Suppose that a particle is charged with q in an electrolyte solution. It is a *kinetic unit* including both the particle and a part of the double layer inside of the shear surface. If an external electric field E_∞ is applied, it exerts a force qE_∞ on the particle (Exercise 10.28). In a steady state, this force must be equal to the viscous force. If the particle is a sphere of radius a the viscous force is given by $4\pi\eta av$ under slip boundary conditions and $6\pi\eta av$ under stick boundary conditions, where η is the viscosity of the solution and v is the particle velocity relative to the solution (see Sec. 4.1).

As pointed out at Eq. 10.77, the boundary condition for the flow may be approximately chosen depending on the thickness of the electric diffuse double layer.

For large κa , the remark at Eq. 10.77 suggests slip boundary conditions. Since the boundary layer is very thin, the polarization charge of the layer outside of the shear surface (outside of the kinetic unit) is negligibly small. Therefore, the potential at the shear surface is just due to the charge q and $\psi_\zeta = q/4\pi\varepsilon_0\varepsilon a$ (Eq. 10.20 cannot be used for $\kappa a \gg 1$) and the electric force is $4\pi\varepsilon_0\varepsilon a\psi_\zeta E_\infty$. This must be equal to the viscous force $4\pi\eta av$. Hence, we have

Fig. 10.7 Electrophoresis ($\kappa a \gg 1$) (Usui, 1995, with permission from the Chemical Society of Japan).



$$v = \frac{\epsilon_0 \epsilon}{\eta} \psi_\zeta E_\infty, \quad (\kappa a \gg 1) \quad (10.83)$$

This result was obtained by Smoluchowski, when the double layer is very thin compared with a .

This problem can also be analyzed in the coordinate system, which is fixed to the particle, so that the solution moves just like in the treatment of the electro-osmosis (see Sec. 10.52). In the case of $\kappa a \gg 1$, the ionic strength of the solution is large and the applied field is distorted around the particle, as shown in Fig. 10.7, even though no modification of the double layer is assumed. As seen in this figure, the applied field is tangential, almost everywhere, to the spherical surface. (Smoluchowski took implicitly this distortion into account.) If so, the surface can be considered to be locally flat and to have the similar configuration as that of the electro-osmosis considered in Sec. 10.5.2. Therefore, Eq. 10.76 with $\kappa x \gg 1$ suggests Eq. 10.83 (Exercise 10.34) and a close relationship between the electro-osmosis and electrophoresis. The viscous force between the sphere and the solution occurs, in this case, only in a very thin layer and outside this layer there is no viscous force. Thus, the motion of the sphere occurs as if it does under slip boundary conditions, as we have obtained Eq. 10.83. It implies that the case of $\kappa a \gg 1$ eliminates complications due to polarization of the diffuse layer.

The quantity, $(\epsilon_0 \epsilon / \eta) \psi_\zeta$, is called the electrophoretic mobility. It is interesting to note that this mobility depends neither on the size of the particle nor the ionic strength of the solution. However, the size is one of the determining factors in choosing the boundary conditions as discussed below.

The ζ -potential is usually measured by electrophoresis. The value of ψ_ζ gives the amount of the charge, q , for the kinetic unit. This q is different from σ_0 of Eq. 10.31.

For $\kappa a \ll 1$, the applied field is not much distorted by the weak double layer around the solid sphere as seen in Fig. 10.8. This small or negligible distortion will be guaranteed if the particle has the same conductivity as that of the solution or is a point particle (very small in size). The flow velocity decays slowly outside the double layer. We can see then that, for $\kappa a \rightarrow 0$ (in a low ionic strength), the flow scheme is just the Stokes flow, being subject to stick boundary conditions. Equation 10.20 gives the ζ -potential as $\psi_\zeta = q / 4\pi \epsilon_0 \epsilon a$. Thus, changing the coordinate system, in which the particle moves with speed, v , we have

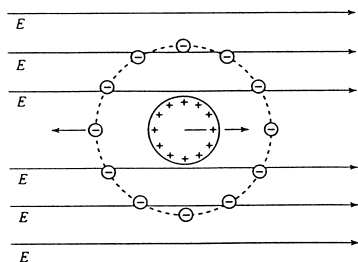


Fig. 10.8 The electric field for $\kappa a \ll 1$ (the retardation effect) (Usui, 1995, with permission from the Chemical Society of Japan).

$$v = \frac{2\varepsilon_0\varepsilon}{3\eta} \psi_\zeta E_\infty, \quad (\kappa a \ll 1) \quad (10.84)$$

This is Hückel's equation.

For a general theory, the phenomenological slip or stick boundary conditions used in Eqs. 10.83 and 10.84 must be treated in terms of Eq. 10.75. In solving the equations, Henry (1931) evaluated the force acting on the double layer per unit volume due to the applied field under the assumption that the double layer is not deformed by the external field (Exercise 10.35). He found that the velocity of the particle is affected by the drag from the electro-osmotic flow. This effect is called the effect of retardation. The effect is small when κa is large, i.e., when electrokinetic effects are less, as we have seen before. However, the effect of retardation becomes larger when κa is small, since the double layer is thick and the electrokinetic effects cannot be ignored. Thus, the effect of the retardation smoothly connects the Smoluchowski's and Hückel's equations. Henry's result is expressed by

$$v = f(\kappa a) \frac{2\varepsilon_0\varepsilon}{3\eta} \psi_\zeta E_\infty \quad (10.85)$$

where $f(\kappa a)$ is called Henry's coefficient and shown in Fig. 10.9.

In the above treatment of the electrophoresis, the distortion of the double layer due to the applied field is not taken into consideration. But, when the ζ -potential is large, the density of co-ions in the double layer is relatively low and the distor-

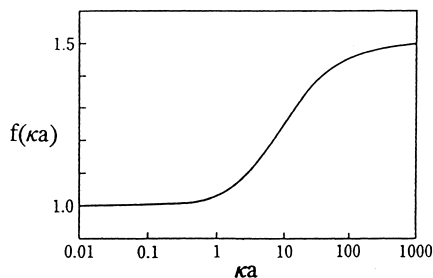


Fig. 10.9 Henry's coefficient.

tion becomes important. The movement of counterions in a direction opposite to that of the particle under the applied field drags the liquid around the particle and causes an accumulation of counterions in the rear side of the particle since the particle is oppositely charged. The electric force due to the counterions acts on the particle to reduce the electrophoretic velocity. This asymmetric accumulation of charges is relaxed by diffusion. Thus, this effect occurs under the balance between the migration and diffusion of counterions, i.e., a relaxation process. Therefore, it is called the effect of relaxation.

In treating theoretically this effect, Overbeek (1943) and Booth (1950) used perturbation methods to expand the variables in terms of the ζ -potential of the particle, and the result is expressed, in Eq. 10.85, replacing $f(\kappa a)$ by $f(\kappa a, \psi_\zeta)$, showing that the relaxation correction is smaller than a few percent if $\psi_\zeta < 25$ mV. For large values of κa , Smoluchowski's equation is good, but the correction is important in the intermediate κa values if ψ_ζ is large. However, the analytical treatment is hard because of the complexity of the problem. O'Brien and White (1978) developed a computational procedure. According to them, for $\kappa a > \sim 6$, the electrophoretic velocity has a peak at around the value of $e\psi_\zeta/k_B T \sim 4$ to 8. If the value of κa is larger, the peak appears at the higher ψ_ζ . If $\kappa a > 250$, the peak occurs at an even higher ψ_ζ value. The reason is, according to O'Brien and Hunter (1981), that, as the ζ -potential increases, the relative density of counterions increases exponentially and the counterions are confined in a layer of diminishing thickness adjacent to the particle surface. On the other hand, for $\kappa a > 10$ and various ζ -potentials Ohshima et al. (1983) presented an analytical expression, which gives correct values within one percent.

In soft particles, like red blood cells, with a surface charge layer, a liquid enters into the layer. Then, their electrophoretic mobilities behave in a different way than those of solid particles (Ohshima and Kondo, 1989). Ohshima (1994) systematically summarized the electrophoretic theories, including soft particles.

The time-dependent diffusion of ion concentration is governed by

$$D\nabla^2 \delta n = \frac{\partial \delta n}{\partial t} \quad (10.86)$$

where D is the diffusion coefficient and δn is the deviation from the equilibrium value. If an alternating field is applied, some interesting behavior of the double layer is observed at two relaxation frequencies: one at around D/a^2 (D being the diffusion coefficient) is associated with building up the ion diffusion layer around the particle, and the other at $\kappa^2 D$ associated the conduction of charge around the double layer.

10.6 Measurement of ζ -potentials

In practical point of view, ζ -potentials play an important role in electrokinetic phenomena as well as in the stability of some disperse systems.

There are various methods of measuring the ζ -potentials of charged particles (Hunter, 1981; Kittaka et al., 1984). Briefly, the electrophoretic mobility of charged particles, the flow volume of a solution due to electro-osmosis, the streaming potential under a pressure gradient, the potential generated by sedimentation of charged particles, the ultrasonic vibration potential (*UVP*), and the electrokinetic sonic amplitude (*ESA*) are typical methods. In particular, the latter two, *UVP* and *ESA*, are promising methods since they can be used in situ at high concentrations.

The velocity of a particle may be measured by means of a microscope if the particle size is larger than $0.5\ \mu\text{m}$ or by an ultramicroscope if the particle size is $0.5\text{--}0.1\ \mu\text{m}$. The particle velocity relative to the surrounding liquid leads to the electrophoretic mobility.

If an aqueous solution is in a glass tube, the surface is negatively charged. If an electric field is applied along the tube, there is, therefore, an electro-osmotic flow. This flow interferes the microscopic measurement of the particle velocity. If the tube is closed at the both ends, there is then a return flow of the solution along the axis of the circular tube. The electro-osmotic flow near the inner surface is in the direction of the electric field, since ρ_f is positive there. The profile of the (electro-osmotic) flow velocity, v_{eosm} , is the famous Poiseuille flow in the cylindrical tube of the inner radius, a ,

$$v_{\text{eosm}} = (v_0/a^2)(2r^2 - a^2) \quad (10.87)$$

where v_0 is the electro-osmotic velocity at the tube wall and r is the distance from the axis (see Fig. 10.10). The total flow through the cross-section of the tube must vanish, since the tube is closed. The flow is at rest on the cylindrical surface $r=r_s$, which is given by

$$r_s = a/\sqrt{2} \quad (10.88)$$

where r_s is called the stationary level. The particle velocity measured at this level is directly related with the mobility.

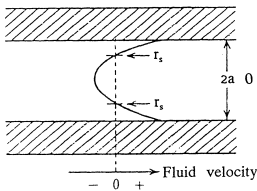


Fig. 10.10 Poiseuille's flow.

Another method is to measure the particle velocity at various points across the cross-section and, then, the area under this velocity profile divided by the cross-sectional area is the electrophoretic velocity, since the net flow of the solution is zero. However, in either case a caution must be taken, so that Joule heating is minimized. The particles should not be too large in order to avoid sedimentation under gravity.

The laser light scattered by a moving particle undergoes a frequency shift by the Doppler effect. The shift may be measured at various levels to measure the mobility. The particle makes also a Brownian motion, which results in the line broadening in addition to the Doppler line shift (Sec. 6.2.2.1). The power density function, $I(\omega)$, of the scattered light is given by

$$I(\omega) = \frac{Dq^2/\pi}{(\omega - \omega_0 + \mathbf{q} \cdot \mathbf{v})^2 + (Dq^2)^2} \quad (10.89)$$

where D is the translational diffusion coefficient of the particle, ω_0 is the frequency of the incident light, and \mathbf{v} is the electrophoretic velocity, if measured at the stationary level. The quantity, \mathbf{q} , is the scattering vector, Eq. 6.10, and $\mathbf{g} \cdot \mathbf{v}$ is the Doppler shift (Sec. 6.2.2.1). If the light is incident perpendicularly to \mathbf{v} , the shift is given by $(2\pi/\lambda)bE_\infty \sin \theta$, where b is the electrophoretic mobility and λ and θ are defined before at Eq. 6.10. Since the shift is very small (~ 100 Hz), the detection is made by beating of heterodyning as discussed in Sec. 6.2.2.4 (Ware and Flygare, 1972; Miller and Yamanchili, 1992).

We must note that ζ -potentials obtained by different methods do not necessarily agree (Zukoski and Saville, 1985).

As noted before, there are many other methods, but the most notable methods are *UVP* and *ESA*, which can be used for solutions of high concentrations. When a ultrasonic wave is passing through a solution, ions more easily vibrate around their equilibrium positions than the charged particle does. Accordingly, a periodic polarization with the period of the ultrasonic occurs and alternating potentials appear spatially separated at every odd number of the half-wavelength of the ultrasonic wave. If the wave is standing, electrodes can be placed at every half-wavelength to measure the potentials, called the ultrasonic vibration potentials (Fig. 10.11). Enderby (1951) gave the following equation for dilute solutions:

$$UVP = \frac{2P}{\rho_1} \frac{\varphi}{\lambda_e} (\rho_p - \rho_1) \frac{\varepsilon_0 \varepsilon \psi_\zeta}{\eta} \quad (10.90)$$

where P is the sound pressure, φ is the volume fraction of the particle (concentration), ρ_p and ρ_1 are the densities of the particle and the liquid, respectively, and λ_e and η are the electric conductivity and the viscosity of the liquid, respectively. If $\rho_p - \rho_1$ is large, the *UVP* is large.

If the concentration is high, Eq. 10.90 needs a correction. According to Levine et al. (1976),

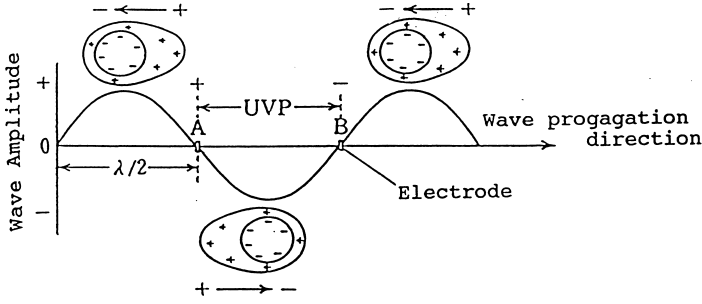


Fig. 10.11 Ultrasonic vibration potential (Marlow et al., 1988, with permission from the American Chemical Society).

$$UVP = \frac{2P}{\rho_1} \frac{\varphi}{\lambda_e} (\rho_p - \rho_1) \frac{\varepsilon_0 \varepsilon \psi_\zeta}{\eta} \frac{g(\kappa a, \varphi)}{G(\varphi)} \quad (10.91)$$

where $g(\kappa a, \varphi)$ is a correction against the interparticle electric interactions and $G(\varphi)$ corrects for the interparticle hydrodynamic interactions. If $\kappa a \gg 1$, Marlow et al. (1988) gave

$$UVP = \frac{2P}{\rho_1} \frac{\varphi}{\lambda_e} (\rho_p - \rho_1) \frac{\varepsilon_0 \varepsilon \psi_\zeta}{\eta} (1 - \varphi) \quad (10.92)$$

The *UVP* measuring instrument is commercially available: Pen-Kem-System-700, which uses a source of the 200 kHz ultrasonic wave.

If a high frequency alternating potential is applied between two electrodes in a solution, an ultrasonic oscillation is generated and this is called the electrokinetic sonic amplitude and can be observed by a piezo detector. This method is developed in 1985 by Maltec Applied Science Co., which commercially provides an instrument named ESA-800. Using the same notations as those in Eq. 10.90, the *ESA* is given by

$$ESA = \varphi(\rho_p - \rho_1) \cdot c \cdot \mu(\omega) \cdot f \quad (10.93)$$

where c is the speed of the sound in the solution and the value of f depends on the shape of the electrodes (usually, $f \sim 1.4$). The factor, $\mu(\omega)$, is called the dynamic mobility and given by a complex function ($i = (-1)^{1/2}$):

$$\mu(\omega) = \frac{\varepsilon_0 \varepsilon \psi_\zeta}{\eta} \left[1 - \frac{i\alpha(3 + 2[\rho_p - \rho_1]/\rho_1)}{9(1 + [1 - i]\sqrt{\alpha/2})} \right]^{-1} \quad (10.94)$$

with $\alpha = \omega a^2 / \nu$, where a is the radius of the particle and ν is the dynamic viscosity of the electrolyte solution.

In the measurement of ζ -potentials, the values obtained by the methods of *UVP* and *ESA* have been proved to be accurate within the experimental errors compared with those obtained by a conventional method, checked with various materials under various values of pH (Hozumi and Furusawa, 1990).

10.7 Electrical Conductivity of Dilute Dispersions

In electrokinetic experiments, the motion of individual charged particles is determined under an external electric field. On the other hand, the averaged behavior of the particles determines the electrical conductivity.

Consider first a suspension of uncharged, non-conducting particles of radius, a , in a medium of conductivity, σ_c . Assume that the dielectric constant of the solution is much larger than that of the particle. Under an external electric field, \mathbf{E}_∞ , the particle is polarized and the potential around it is

$$\psi_{\text{out}} = -(1 + Ar^{-3})\mathbf{x} \cdot \mathbf{E}_\infty \quad (10.95)$$

where $A = a^3/2$. The potential inside the particle is

$$\psi_{\text{in}} = -(3/2)\mathbf{x} \cdot \mathbf{E}_\infty \quad (10.96)$$

The effective conductivity, σ_c^{eff} , is defined from the average current density and the averaged electric field, as follows.

$$\mathbf{J} = \langle \mathbf{j} \rangle = \sigma_c^{\text{eff}} \langle \mathbf{E} \rangle \quad (10.97)$$

where \mathbf{j} and \mathbf{E} are the local spatially fluctuating current and field because of the polarizable particles. The averages, \mathbf{J} and $\langle \mathbf{E} \rangle$, are measureable. The local fields are related by the local conductivity. But note that the particles are non-conducting. Therefore, the local conductivity is that for the fluid, σ_c , outside of the particles. The averaging processes are given by

$$\mathbf{J} = \frac{1}{V} \int_V \mathbf{j} dV \quad \text{and} \quad \langle \mathbf{E} \rangle = \frac{1}{V} \int_V (-\nabla \psi) dV$$

where the integrations are over a volume, V , containing the solution and particles.

The average field, $\langle \mathbf{E} \rangle$, is the average of the field outside particles (due to Eq. 10.95) and the field inside particles (due to Eq. 10.96) within the volume, V . Note that the second term of Eq. 10.95 does not contribute to the average because of symmetry. Therefore, $\langle \mathbf{E} \rangle = (1 + 1/2\varphi)\mathbf{E}_\infty$, where φ is the volume fraction of par-

ticles. The extra field comes from polarization of individual particles. The current density, \mathbf{J} , is given similarly by $\langle \mathbf{j} \rangle = \sigma_c(1-\varphi)\mathbf{E}_\infty$ from Eq. 10.95. Hence,

$$\mathbf{J} = \sigma_c^{\text{eff}} \langle \mathbf{E} \rangle = \sigma_c \left(1 - \frac{3}{2} \varphi \right) \langle \mathbf{E} \rangle \quad (10.98)$$

If the particles consist of material of conductivity σ_p , so that they are conducting, according to Maxwell (1973), σ_c^{eff} must satisfy

$$\frac{\sigma_c - \sigma_c^{\text{eff}}}{\sigma_c^{\text{eff}} + 2\sigma_c} = \frac{\sigma_c - \sigma_p}{\sigma_p + 2\sigma_c} \varphi \quad (10.99)$$

If the particles are charged, but still non-conducting, there are double layers around the particles. The calculation of σ_c^{eff} can then be made in nearly the same way as above. But complications arise from motion of the particles, variation in ion densities within the double layers, and polarization of ion clouds. The procedures to handle these problems have been shown, for instance, by Saville (1979, 1983). The local current can be written (see Eq. 10.75)

$$\mathbf{j} = \sum_{k=1}^N [e z_k n_k \mathbf{v} - b_k (e^2 z_k^2 n_k \nabla \psi + e z_k k_B T \nabla n_k)] \quad (10.100)$$

In order to obtain $\langle \mathbf{j} \rangle$ ($=\mathbf{J}$) and $\langle \mathbf{E} \rangle$ ($=-\langle \nabla \psi \rangle$), we need \mathbf{v} , n_k , and ψ , which should be obtained by solving the set of equations, Eq. 10.75 (see O'Brian (1981) or Saville (1983) for details.)

In experiments, particles must be carefully cleaned and fully characterized in conduction measurements, since contaminants strongly affect the results. Zukoski and Saville (1985) made the test of the theory of electrical conductivity by measuring σ_c^{eff} as a function of φ and comparing ζ -potentials with those obtained by mobility measurements, showing some discrepancies.

Exercises

10.1 Consider that a permanent electric dipole moment \mathbf{p} at \mathbf{x} is exposed to an electrostatic field $\mathbf{E}(\mathbf{x})$. Show that the electrostatic energy is given by $-\mathbf{p} \cdot \mathbf{E}(\mathbf{x})$ and the force acting on an electric dipole moment \mathbf{p} is given by $\mathbf{p} \cdot \nabla \mathbf{E}(\mathbf{x})$. Which direction the force is oriented? A continuous polarizable solid medium is exposed to $\mathbf{E}(\mathbf{x})$. If $\mathbf{P}(\mathbf{x})$ is the polarization vector, what is the force acting on the medium per unit volume? (Note that \mathbf{P} is the dipole moment per unit volume.)

10.2 Derive Eq. 10.4.

- 10.3** Using the Poisson equation, rewrite $\rho_f E$, the result of which is used in deriving Eq. 10.8. (Equation 10.75 expresses important factors for causing an current.)
- 10.4** Obtain Eq. 10.10.
- 10.5** Under what condition can there be no net electric current in an electrolyte solution of only two components?
- 10.6** How will Eq. 10.15 be modified when there is an electric current? How difficult is it to obtain the general relation? How could it be in the limit of $j \rightarrow 0$?
- 10.7** Show that the value of the Debye-Hückel parameter is given by, for water at 25°C,

$$\kappa^2 = (3.288)^2 I \text{ nm}^{-2}$$

where I is the ionic strength $(= (1/2) \sum c_k z_k^2)$, where c_k is the ionic concentration in mol L^{-1} .

- 10.8** Establish Eq. 10.20.
- 10.9** Why could the van der Waals interaction be more important compared with the Coulombic interaction at a short distance from the surface? Is the surface responsible for the importance? Or, is it also so if just two particles are close to each other?
- 10.10** Derive Eq. 10.21.
- 10.11** Integrate Eq. 10.21 to find Eq. 10.22.
- 10.12** Integrate Eq. 10.22 to find Eq. 10.23.
- 10.13** Consider an electrolyte on the right of a flat surface at a given low potential, $\psi(0)$. Solve Eq. 10.18 for the flat surface, located at $x=0$.
- 10.14** Water molecules at the surface of a solid seem to be oriented, so that their dipole moments do not contribute to the dielectric constant at low temperature. Can you assume then that the dielectric constant of water at the surface is closely related to the optical refractive index of water?
- 10.15** Show that for an asymmetrical electrolyte Eq. 10.16 leads to

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{2k_B T}{\epsilon_0 \epsilon} \sum n_k^0 \left[e^{-\frac{z_k e \psi}{k_B T}} - 1 \right]$$

and the relation, Eq. 10.25, gives

$$\sigma_d = -\frac{\psi_d}{|\psi_d|} \left(2\epsilon_0 \epsilon k_B T \sum n_k^0 \left[e^{-\frac{z_k e \psi_d}{k_B T}} - 1 \right] \right)^{1/2}$$

- 10.16** Establish Eq. 10.32.
- 10.17** Establish Eqs. 10.34 and 10.35.
- 10.18** Noting that $\mathbf{E} = -\nabla\psi$ and $\nabla \cdot (\epsilon_0 \epsilon \mathbf{E}) = \rho_f$, show that Eq. 10.1 can be written as follows.

$$U = \frac{1}{2} \int \rho_f \psi dV$$

- 10.19** Establish Eq. 10.41 and evaluate the integral when $\psi_{H/2}$ is sufficiently small, so that Debye-Hückel approximation can be used.
- 10.20** Consider that a thin metallic plate is located at the distance of separation of $2D$ in front of a semi-infinite solid of the same metal as the metallic plate. The plane surface of the semi-infinite solid is parallel to the thin metallic plate. The remaining

space is filled by a solution of a symmetrical electrolyte. Calculate the repulsive force acting on the metallic plate per unit area.

- 10.21** Apply the Debye-Hückel approximation to the interaction of double layers of two parallel plates with a constant surface potential ψ_0 , so that Eq. 10.18 may be solved under $\psi = \psi_0$ at $x=0$ and H , H being the distance between the plates. Find the force between the plates per unit area and show that the energy of repulsion per unit area is given by

$$\Delta G_R(H) = \frac{2n^0 k_B T}{\kappa} \left(\frac{ze\psi_0}{k_B T} \right)^2 \left(1 - \tanh \frac{\kappa H}{2} \right) = \frac{4n^0 k_B T}{\kappa} \left(\frac{ze\psi_0}{k_B T} \right)^2 \frac{e^{-\kappa H}}{1 + e^{-\kappa H}}$$

- 10.22** Consider the same problem as Exercise 10.20, but with the boundary conditions that the surface charge densities, σ_0 , on the plates are constant. Find the force between the plates per unit area and show the energy of repulsion per unit area is given by

$$\Delta G_R^\sigma = \frac{\sigma_0^2}{\epsilon_0 \epsilon} \frac{1 + e^{-\kappa H}}{\sinh \kappa H}$$

- 10.23** Consider two dissimilar flat plates, A and B, with double layers between them. The potentials, ψ_A and ψ_B , are given ($\psi_A > \psi_B > 0$). At what distance of separation between them is the repulsive force maximum? Show that the plate B is uncharged in this case.

- 10.24** Obtain Eq. 10.46. And find the surface charge densities on the plates, A and B. Remark: the results are

$$\sigma_A = \epsilon_0 \epsilon (\psi_A \coth \kappa h - \psi_B \operatorname{cosech} \kappa h)$$

$$\sigma_B = \epsilon_0 \epsilon (\psi_B \coth \kappa h - \psi_A \operatorname{cosech} \kappa h)$$

(See Eq. 10.46.)

- 10.25** Rewrite Eq. 10.42 by finding $\psi_{H/2}$ from Eq. 10.46.

- 10.26** The force between two flat plates is given by $-d\Delta G_R/dh$. Use Eq. 10.48 to show that

$$F = \frac{-\epsilon_0 \epsilon \kappa^2}{2 \sinh \kappa h} [(\psi_A^2 + \psi_B^2)(\operatorname{cosech} \kappa h - 2\psi_A \psi_B \coth \kappa h)]$$

- 10.27** Find the electrophoretic mobility under stick boundary conditions.

- 10.28** For simplicity, consider a conducting sphere carrying a charge, q , immersed in an electrolyte solution. Use Eq. 10.13 to find the force acting on the charged sphere when an external field, E_∞ , is applied.

- 10.29** Obtain Eqs. 10.76 and 10.77.

- 10.30** Show that the streaming potential is constant over the cross-section of the tube.

- 10.31** In Eq. 10.80, show that the electric field E is uniform on the cross-sectional area of the tube.

- 10.32** In Eq. 10.80, the contribution of the double layer is ignored. For a symmetrical electrolyte in which both species of ions have the same mobility, the exact relation for I' is

$$I' = \left[2\pi \int_0^a \lambda \frac{n_+ + n_-}{2n^0} r dr \right] E + 2\pi \int_0^a \rho_f v r dr$$

where n_+ and n_- are the equilibrium ion densities and v is the osmotic velocity due to the streaming field E . Evaluate I' when the Debye-Hückel approximation holds.

10.33 Establish Eq. 10.81.

10.34 Using Eq. 10.76, obtain the viscous force per unit area acting on the flat plate. Then, by integrating over a spherical surface of radius a , show Eq. 10.83.

10.35 Under a perturbation due to an external field, the charge and the potential in the double layer are, in general, written as $\rho_f^0 + \delta\rho_f$ and $\psi^0 + \delta\psi$, respectively, where quantities with superscript, 0, stand for equilibrium values and those with δ are deviation from them. The force on the free charge due to the electric field is $-\rho_f \nabla \psi$. Show that the first order variation of the force is represented by $-\rho_f^0 \nabla \delta\psi$ for low ζ -potentials, since $-\delta\rho_f \nabla \psi^0$ is of the second order in small ψ_ζ . (Note that $\delta\rho_f \sim -\epsilon_0 \epsilon \nabla^2 \delta\psi$.) Thus, for small ψ_ζ , $\delta\psi$ is more important than $\delta\rho_f$ and this deviation of ψ may be introduced in Eq. 10.75 to calculate $f(\kappa a)$.

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